Thermal conductivity via magnetic excitations in spin-chain materials

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We discuss the recent progress and the current status of experimental investigations of spin-mediated energy transport in spin-chain and spin-ladder materials with antiferromagnetic coupling. We briefly outline the central results of theoretical studies on the subject but focus mainly on recent experimental results that were obtained on materials which may be regarded as adequate physical realizations of the idealized theoretical model systems. Some open questions and unsettled issues are also addressed.

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1. INTRODUCTION

Heat transport in solids is often very sensitive to even weak disorder and is significantly influenced by phase transitions. That is why measurements of the thermal conductivity are an efficient experimental tool in solid state physics. Several books and review articles were devoted to thermal conduction in solids.[1,2,3,4] These previous authors usually discussed the heat transport by two species of itinerant quasiparticles only, i.e., by considering the thermal conductivity by phonons (κ_{ph}) and by itinerant charge carriers (κ_e). Even when dealing with magnetic systems, the influence of magnetic excitations is typically seen in a reduction of the phonon and electron thermal conductivities via scattering of these quasiparticles by magnons or magnetic impurities. The heat transport via the spin system itself was, to a large extent, neglected. One of the main reasons for this imbalance is that usually, it is very difficult to separate the spin contribution (κ_s) from the total measured thermal conductivity which, in most cases, is dominated by phonon heat transport. This problem is particularly severe for antiferromagnetic (AFM) three-dimensional (3D) materials where the linear dispersion

of the spin excitations causes, at low enough temperatures, κ_s to adopt a T^3 dependence, the same as $\kappa_{\mathrm{ph}}(T)$. A much more favorable situation is met in strongly anisotropic spin systems, such as spin-chain materials, where the exchange interaction along a particular direction is much stronger than perpendicular to it. Since no thermal conductivity via spin excitations is expected perpendicular to the chain direction, investigating the anisotropy of the heat transport is an efficient method for the identification of κ_s. What really makes spin-chain materials very attractive objects for transport measurements is, however, the influence of quantum effects on their properties, which are most pronounced for low spin values ($S = 1/2$ and $S = 1$).

Unusual transport of energy and magnetization in certain 1D quantum spin systems was predicted long ago.[5,6,7,8] More recent theoretical studies along these lines induced a revival of interest in unusual transport properties of integrable spin systems.[9,10,11,12] During the last decade, many new results have been obtained for transport properties of various 1D quantum spin models, not only for the "simple" case involving an isotropic nearest-neighbor interaction, but also taking into account higher-order neighbor interactions, frustration effects and coupling to phonons. In addition, more complex 1D spin arrangements such as ladders and zig-zag chains were considered. The resulting theoretical progress was reviewed in recent articles 13,14. This progress, linked to recent advances in preparation of materials whose features seem to fulfill some of the assumptions of the various idealized models quite well, has led to a considerable activity in experimental studies of heat conduction in 1D spin systems. A corresponding summary of earlier activities was given in Ref. 15.

In this article, we present a brief survey of recent experimental results on the thermal conductivity via excitations in 1D AFM spin systems. Heat transport in the 3D ordered spin state caused by weak yet unavoidable interchain interactions is not discussed here since it allows for a conventional description in terms of well-defined quasiparticles (magnons). We do not attempt to provide a full account of all the published papers on thermal conductivity of spin-chain materials, but rather concentrate on several central topics where some experimental progress has recently been achieved. First, we discuss whether the observed thermal transport in spin-chain compounds indeed reflects the expectations that emerged from the mentioned theoretical work. Then, we discuss what type of information on perturbations affecting the spin-mediated transport can be extracted from recent experimental data. Since most of the model materials are insulators, the dominating influence is due to the interaction of the spin system with phonons as well as with magnetic defects. Another issue that we address here is how the predicted relations between thermal conductivity and spin conductivity in

low-dimensional spin systems were attempted to be verified in recent experiments. Finally, we discuss some features of the thermal conductivity of spin chains in external magnetic fields.

2. THERMAL TRANSPORT IN SPIN CHAINS AND LADDERS

2.1. Is it anomalous?

In the modern theoretical literature, the energy transport in 1D spin systems has been addressed employing either the Boltzmann transport equation formalism or the linear response formalism. The former approach, which relies on the notion of quasiparticle modes with associated velocities and relaxation times, provides transparent results and is well suited for the analysis of experimental data. However, this quasiparticle picture is not always applicable for quantum many-body systems. Thus, the most widely used approach was directed towards the calculation of transport coefficients via time-dependent current-current correlation functions, due to Kubo.[16] For the thermal conductivity at a finite frequency ω,[17]

$$\kappa(\omega) = \frac{1}{T} \int_0^\infty dt e^{-i\omega t} \int_0^{1/T} d\tau \langle j_{\text{th}}(-t - i\tau) j_{\text{th}} \rangle, \qquad (1)$$

where j_{th} is the energy current and $\langle ... \rangle$ denotes the thermodynamic average. The real part of Eq. (1) can be decomposed into

$$\operatorname{Re} \kappa(\omega) = D_{\text{th}} \delta(\omega) + \kappa_{\text{reg}}(\omega), \qquad (2)$$

where the weight of the singular part (D_{th}) is the so-called thermal Drude weight. The experimentally accessible quantity is the dc conductivity $\operatorname{Re} \kappa(\omega \to 0)$. A nonzero D_{th} implies a non-decaying energy current and, thus, ballistic heat transport. Since the energy current is one of the conserved quantities,[9,11,18] the existence of a nonzero Drude weight is often linked with the integrability of a system. The question whether D_{th} may, for various spin systems, adopt a nonzero value and how it evolves under the influence of different perturbations are the central points of current theoretical studies of thermal transport in quantum spin systems. The thermal Drude weight $D_{\text{th}}(T)$ is as important for thermal transport as is the Drude weight $D(T)$ for electric transport where its value at $T = 0$ distinguishes an ideal conductor $(D(0) > 0)$ from an insulator $(D(0) = 0)$, as was put forward by Kohn.[19] Extending Kohn's conjecture to heat transport and to nonzero temperatures,[9] several cases can be distinguished:

(a) thermal insulators if $D_{\text{th}}(T) = 0$ and $\kappa_{\text{reg}}(\omega \to 0, T) = 0$;

(b) conventional thermal conductors if $D_{\text{th}}(T) = 0$ and $\kappa_{\text{reg}}(\omega \to 0, T) > 0$;

(c) ideal thermal conductors if $D_{\text{th}}(T) > 0$ for any value of $\kappa_{\text{reg}}(\omega \to 0, T)$.[13]

However, an experimentally observed, anomalously large *dc* thermal conductivity does not necessary imply a ballistic thermal transport (case (c)). It is also possible that, even if $D_{\text{th}}(T) = 0$ (case (b)), the low-ω part of $\kappa_{\text{reg}}(\omega, T)$ may adopt anomalously large values for certain systems with slowly decaying energy currents. Even if calculations for an idealized pure system suggest the existence of a nonzero Drude weight, in any real system, perturbations such as phonons, 3D couplings, or defects may destroy the integrability of the system. As a result, the δ-peak broadens into a Lorentzian with a width inversely proportional to the relaxation time $\tau(T)$, the value of which depends on the type and strength of the perturbation, and the thermal conductivity is reduced accordingly. Thus, only a comparison of experimental data with theoretical calculations, taking into account both the singular and the regular parts of the conductivity spectrum, provides a reliable judgement of the situation.

Real materials of current interest which may be regarded as reasonable physical realizations of model low-dimensional spin S systems belong to three classes: $S = 1/2$ chains, $S = 1$ chains, and two-leg $S = 1/2$ ladders. An often encountered case is the Heisenberg $S = 1/2$ XXZ chain, for which the Hamiltonian is

$$H = J \sum_i (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \Delta S_i^z S_{i+1}^z), \tag{3}$$

where $J > 0$ is the intrachain nearest-neighbor exchange coupling and Δ characterizes the anisotropy of the interaction. The excitations are pairs of $S = 1/2$ quasiparticles (spinons) and the spectrum consists of a continuum with an upper and a lower boundary. It is gapless for $|\Delta| \leq 1$ but a spin gap opens for larger $|\Delta|$. The isotropic case $\Delta = 1$ is especially important because a number of model systems with J ranging from quite high (e.g., Sr_2CuO_3 with $J/k_B \approx 2000$ K)[20] to rather low values (CuPzN with $J/k_B \approx 10$ K)[21] have been realized in appropriate material syntheses. Systems which are described by Eq. (3) are integrable for $|\Delta| < 1$ (easy plane) as well as for $\Delta = 1$ (isotropic). In several theoretical papers and using different methodical approaches it has unambiguously been demonstrated that at $T > 0$, the thermal Drude weight is nonzero if $|\Delta| \leq 1$.[22,23,24,25] Other work established the thermal transport in $S = 1/2$ chains in the gapped phases, such as XXZ chains with Ising-type anisotropy $|\Delta| > 1$,[26] with next-nearest neighbor interactions,[27] with three-spin interactions,[28] with dimerization and frustrations.[23,24,29,30] For $T > 0$, some calculations predicted a

nonzero D_{th} in the massive regime;[24,26,30] other studies question this con-
clusion for dimerized and frustrated chains, however.[23,31]

The same uncertainty about $D_{\text{th}}(T > 0)$ exists for $S = 1$ chain systems.
The excitation spectrum of the isotropic AFM $S = 1$ model has a large
gap; the system is nonintegrable. Although earlier calculations provided
support for a nonzero thermal Drude weight at all temperatures,[24] more
recent work suggests that $D_{\text{th}}(T)$ vanishes in the thermodynamic limit.[32] In
the latter case, the thermal conductivity of the spin system is expected to
be completely governed by the regular contribution $\kappa_{\text{reg}}(\omega, T)$.

A great deal of recent theoretical interest concentrated on the trans-
port properties of two-leg $S = 1/2$ ladders. This interest was stimulated
by experimental observations of a rather large spin thermal conductivity
along the ladder direction in variants of $(\text{Ca,Sr})_{14}\text{Cu}_{24}\text{O}_{41}$ which contains
spin ladders as a structural element.[33] The ladders are $S = 1/2$ chains (legs)
connected in pairs, with an exchange constant J along the legs and $J_\perp$ per-
pendicular to the legs (along the rungs). The interaction along the rungs
is the integrability-breaking perturbation because for $J_\perp = 0$, the system
is just a set of $S = 1/2$ chains as described above. For $J_\perp > 0$, the situ-
ation with the thermal Drude weight is controversial, similar to other non-
integrable systems with spin gaps mentioned above: the nonzero thermal
Drude weight calculated for this system disagrees with more recent numeri-
cal calculations.[24,31,34,35]

Measurements of the thermal conductivity were made for several phys-
ical realizations of 1D spin systems. Before discussing the experimental
results for κ_s, we wish to mention some aspects of ambiguity in the data
analysis. The standard method of measuring the components of the thermal
conductivity tensor κ relies on the Fourier law of proportionality

$$\mathbf{J}_{\text{th}} = -\kappa \nabla T, \tag{4}$$

linking the heat flux $\mathbf{J}_{\text{th}}$ and the temperature gradient ∇T. The heat flux
is typically directed along one of the main crystallographic axes, e.g. α,
therefore we consider $\kappa_{\alpha\alpha} \equiv \kappa^\alpha$. The measured thermal conductivity always
includes contributions from all delocalized excitations acting as heat carriers.
Therefore, separating the spin thermal conductivity κ_s from contributions
of phonons κ_{ph}, electronic quasiparticles κ_e etc., is, in general, not straight-
forward. Although κ_e is negligibly small or zero for most studied spin-chain
compounds, the phonon contribution is always larger or, at least, of the same
order of magnitude as κ_s. In principle, one may try to reduce κ_{ph} by intro-
ducing some lattice defects which scatter phonons much stronger than spin
excitations. This step has successfully been applied to the spin-ladder com-
pounds $(\text{Sr,Ca,La})_{14}\text{Cu}_{24}\text{O}_{41}$.[36] Unfortunately, the deliberately introduced

disorder produces some unavoidable additional scattering of spin excitations as well.

The most widely used approach for establishing κ_s exploits the fact that, because of very weak interchain interactions, the spin contribution to the transport perpendicular to the chains is usually negligible. Thus, for establishing the spin contribution one has to compare the thermal conductivity $\kappa^{\parallel}$ measured parallel to the chains (which contains both κ_{ph} and κ_s) with the thermal conductivity $\kappa^{\perp}$ perpendicular to the chains (which contains only κ_{ph}). Still, because of the possible anisotropy of phonon transport, this method is, in some cases, only partly successful in avoiding substantial uncertainties in the evaluation of $\kappa_s(T)$. This is especially the case in the vicinity of phase transitions, where the phonon scattering by critical fluctuations is often very strong and not necessarily isotropic. For example, the existence of thermal conduction via the spin system was discussed for the $S = 1/2$ chain cuprate $CuGeO_3$.[37,38,39,40] Here the Cu atoms are linked via superexchange with J_c=10.4 meV along the chain direction (c axis), while in the perpendicular directions, the coupling is at least an order of magnitude weaker ($J_b \sim 0.1J$ and $J_a \sim -0.01J$).[41] The temperature dependence of the thermal conductivity $\kappa^{\parallel}(T)$ along the chain direction exhibits a two-peak structure. It has been speculated that the higher-temperature peak is caused by the spin contribution to $\kappa^{\parallel}(T)$, while the lower-temperature peak is of phononic origin.[37,38] However, the same features are also observed for $\kappa^{\perp}(T)$, where κ_s is expected to be negligible.[38,42] Taking into account that the spin-Peierls transition occurs exactly between the two peaks at $T_{SP} \approx 14$ K, the two-peak feature may safely be attributed to phonon transport with enhanced scattering close to the transition.[43,44,42] As a result, despite the large amount of experimental work on thermal transport in $CuGeO_3$, the identification of spin-carried heat conduction in this material has not been established unequivocally. A similar situation is met for the S = 1/2 chain compounds $KCuF_3$ and $BaCu_2Si_2O_7$. Because of moderately weak interchain interactions, the 3D magnetic ordering sets in at relatively high temperatures (39.8 K and 9.2 K for $KCuF_3$ and $BaCu_2Si_2O_7$, respectively) and is reflected in the temperature dependences of κ_{ph} and κ_s.[45,46]

Only when the temperature dependences of the thermal conductivities perpendicular to the chains are smooth and featureless, they can be used for evaluating the phonon background parallel to the chains. Examples are shown in Fig. 1. For the two materials, $\kappa^{\perp}(T)$ exhibits a single peak at low temperatures and, at elevated temperature, $\kappa^{\perp}(T)$ varies approximately as T^{-1} which is typical for phonon thermal conduction of nonmagnetic insulators.[1] In turn, the thermal conductivity parallel to chains $\kappa^{\parallel}(T)$ shows, on top of the phonon contribution, a distinct additional fea-

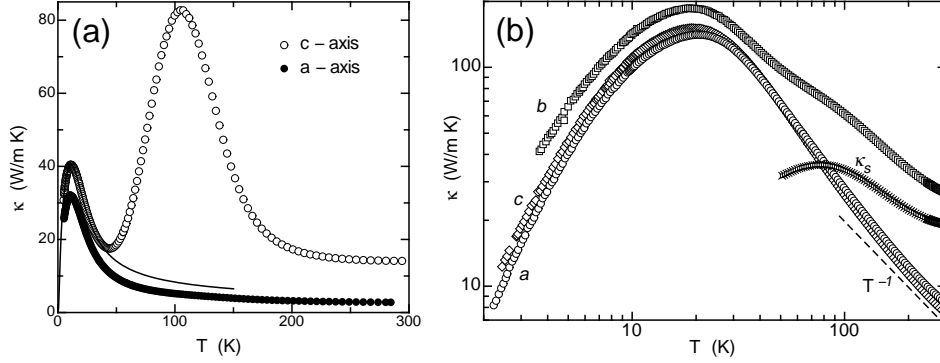**Thermal conductivity in spin-chain materials**

Fig. 1. (a) Thermal conductivity of the spin-ladder compound $Sr_{14}Cu_{24}O_{41}$.[33,47] The ladders are parallel to the c axis. (b) Thermal conductivity of the $S = 1/2$ chain material Sr_2CuO_3.[48] The chains run parallel to the b axis.

ture at higher temperatures. These extra contributions were attributed to thermal transport via the spin system, represented by $\kappa_s(T) \equiv \kappa_s^{\parallel}(T)$. The phonon background $\kappa_{\mathrm{ph}}^{\parallel}(T)$ can be analyzed and subtracted from $\kappa^{\parallel}(T)$ but it is obvious that the uncertainties in $\kappa_s(T)$ are large for temperatures where the phonon background dominates.

If we now turn to the experimental results so far obtained for $\kappa_s(T)$, the main question is whether these results are consistent with the ballistic heat transport expected for integrable systems. If we define ballistic transport as transport where the mean free path of the excitations is limited by the sample dimensions, then the answer would be negative. The mean free path l_s of 1D spin excitations can roughly be evaluated using the kinetic equation

$$\kappa_s(T) = C_s(T)v_s(T)l_s(T), \tag{5}$$

where C_s is the magnetic specific heat and v_s is the mean velocity of spin excitations. The data for $l_s(T)$ are available for $S = 1/2$ chain materials, such as Sr_2CuO_3,[48] $SrCuO_2$,[49] $BaCu_2Si_2O_7$,[46] $CuGeO_3$,[37,38,39] Yb_4As_3,[50] as well as for the $S = 1$ chain materials $AgVP_2S_6$,[51] and Y_2BaNiO_5,[52] and some variants of the $S = 1/2$ two-leg ladder compound $(Ca,Sr,La)_{14}Cu_{24}O_{41}$.[33,36] In all cases, l_s was never larger than a few 10^3 Å, much shorter than the lateral extensions of typical samples which were of the order of 1 mm.

However, a more general definition of ballistic transport is provided by the presence of non-decaying contributions to the energy current which can be shown to be equivalent to the existence of a nonzero Drude weight. This definition is more appropriate because it does not rely on the validity of the quasiparticle approach. Applying this criterion in analyzing the

experimental results of steady-state heat transport experiments, the identification of the ballistic transport relies on demonstrating that the measured κ_s exceeds the values of the thermal conductivity provided by the regular contribution in Eq. (2). Experimental data available in the literature indeed seem to support the theoretical predictions which claim ballistic thermal transport in $S = 1/2$ uniform Heisenberg chains and diffusive transport in $S = 1$ chains. In Fig. 2, we plot the spin-related energy diffusion constants D_E that were calculated from experimental data of $\kappa_s(T)$ for several spin-chain compounds[52] by using $D_E(T) = \kappa_s(T)/(C_s(T)a^2)$, where $C_s(T)$ is the specific heat of the spin chain and a the lattice constant along the chains. For $S = 1$ chains, the energy diffusion constant has recently been calculated from the regular contribution $\kappa_{\mathrm{reg}}(\omega, T)$ for high temperatures.[32] The high-temperature limiting value D_E^{ht} is indicated by an arrow in Fig. 2. For both $S = 1$ compounds presented in Fig. 2 the energy diffusion constants are clearly of the same order of magnitude as D_E^{ht} values. In contrast, $D_E(T)$ for the $S = 1/2$ chains are much larger than for the $S = 1$ species, they exhibit a strong temperature dependence and do not scale with T/J, as one would expect for diffusion that is governed by intrinsic interactions only. Taking into account that the theory predicts $\kappa_{\mathrm{reg}}(\omega, T) = 0$ for $S = 1/2$ chains in the gapless regime, this comparison strongly suggests that intrinsic diffusion is the dominating process in $S = 1$ chains but much less so in $S = 1/2$ chains. A comparison between calculated values of $\kappa_{\mathrm{reg}}(\omega, T)$ and experimental results for $\kappa_s(T)$ has recently been made for two-leg spin ladders.[35] This comparison suggests that the experimentally observed thermal conductivity via the spin system is governed by intrinsic diffusion. The emerging understanding of the dichotomy between diffusive and ballistic transport in 1D spin systems is that the thermal transport in systems with a spin gap, such as $S = 1$ chains or $S = 1/2$ even-leg ladders, is determined by intrinsic diffusion, while for $S = 1/2$ spin chains with gapless spectra, the thermal transport is ballistic and limited by external perturbations.

2.2. Scattering mechanisms

Although most of the relevant theoretical work was based on the Kubo formalism, the analysis of experimental data on the thermal conductivity of low dimensional spin systems is usually employing Boltzmann's kinetic transport theory. In this approximation

$$\kappa_s = \sum_k \frac{df(k,T)}{dT}\varepsilon(k)v_s(k)l_s(k,T), \tag{6}$$

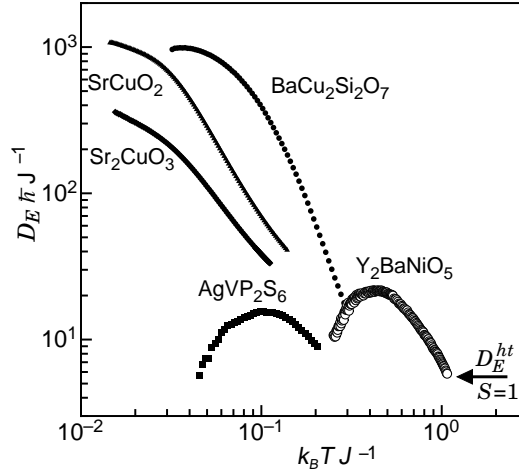**Thermal conductivity in spin-chain materials**

Fig. 2. The energy diffusion constant $D_E(T)$ calculated from the thermal conductivity data of the $S = 1$ chain compounds $AgVP_2S_6$ and Y_2BaNiO_5, and of the $S = 1/2$ chain compounds $BaCu_2Si_2O_7$ and $SrCuO_2$ (data from Refs. 46,49,51,52). The arrow corresponds to the high-temperature limit D_E^{ht} calculated for $S = 1$ chains in Ref. 32.

where f, ε, v_s, and l_s are, respectively, the distribution function, the energy, the velocity, and the mean free path of spin excitations with wavevector k. The mean free path l_s is related to the relaxation time τ as $l_s = v_s\tau$. Assuming that several scattering mechanisms act independently of each other, in most cases a good approximation for the total mean free path is

$$l_s^{-1}(k, T) = \sum_i l_{s,i}^{-1}(k, T), \tag{7}$$

where each $l_{s,i}(k, T)$ term corresponds to an independent scattering channel. In order to keep the analysis tractable, in most experimental papers it is usually assumed that the scattering rates are k-independent, such that $l_{s,i}(k, T) \equiv l_{s,i}(T)$. This assumption is often questionable but largely dictated by the lack of properly developed theoretical formalisms describing the relevant scattering processes of spin excitations in 1D systems. Nevertheless, it is very useful in the sense that it allows to use the simplified expression of Eq. (5) to estimate the values and the temperature dependence of the average mean free path of excitations in the corresponding spin system.

In many experimental publications on the spin thermal conductivity in 1D spin chains and ladders,[39,33,49,36,50,53,46,52,40,54,55,56,57] magnetic defects were considered as major scattering centers for spin excitations. It was always assumed that the corresponding scattering rates and hence the mean
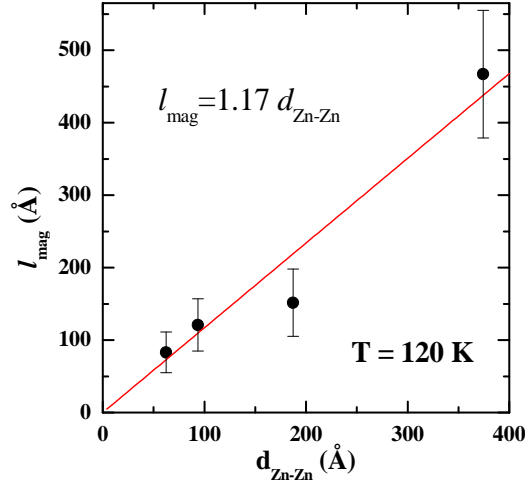
Fig. 3.   Magnon mean free path as a function of the mean distance between Zn ions along the ladders d_{Zn-Zn} in $Sr_{14}Cu_{24-x}Zn_xO_{41}$ (from Ref. 57).

free paths ($l_{s,\text{def}}$) were T- and k-independent. In several studies, the influence of intentionally introduced disorder on the mean free path of spin excitations was investigated.[39,40,53,56,57] It was shown that the reduction of $l_{s,\text{def}}$ indeed correlates with the concentration of magnetic defects, as is illustrated in Fig. 3 for the spin-ladder compound $Sr_{14}Cu_{24}O_{41}$ with Zn serving to partially replace Cu on the corresponding sublattice.[57] Analogous correlations of the values of $l_{s,\text{def}}$ with the concentration of defects, estimated from NMR and magnetic susceptibility measurements, were reported in Refs. 48,52.

There is no doubt that magnetic defects are very effective scatterers of spin excitations in 1D magnetic systems. However, the convenient assumption that $l_{s,\text{def}}$ is T- and k-independent, seems not to be justified in general. The scattering of spin excitations by impurities and disorder was addressed theoretically in Refs. 58,59 for gapless $S = 1/2$ chains. The calculations suggest that the impurity relaxation time (and thus $l_{s,\text{def}}$) should be proportional to temperature. In Ref. 24, the scattering by impurities was analyzed for 1D spin systems with a gap in the excitation spectrum. It was found that the lifetime of spin excitations is energy dependent for the single-impurity case, and the situation is even more complicated for higher concentrations of impurities.

Another species of scatterers needs to be taken into account in analyzing the data for the spin-ladder compound $(Ca,Sr)_{14}Cu_{24}O_{41}$ where, depending on the chemical composition, different concentrations of mobile holes are present in the ladders. In Ref. 33 it was suggested that in $Sr_{14-x}Ca_xCu_{24}O_{41}$ $(x = 0, 2)$ the holes are the principal scatterers of magnons at high tem-

peratures. This conclusion was based on the observation that l_s correlates with the average distance between holes. Subsequent experiments on $(Ca,Sr)_{14}Cu_{24}O_{41}$ provided additional supporting evidence for the magnon-hole scattering in this material.[36,54] The holes are considered as a kind of mobile defects which scatter magnons in the same way as static defects, thus providing a T- and k-independent term to the total inverse mean free path if the concentration of holes does not vary with temperature. At low temperatures, this assumption is not valid because the holes either adopt an ordered configuration or are transferred out of ladders.[54]

At not very low temperatures, the scattering of spin excitations by phonons is expected to be significant. This scattering mechanism was taken into account in the analyses of experimental results for several spin-chain and spin-ladder materials by including a term $l_{s,\mathrm{ph}}^{-1}(T)$ on the right-hand side of Eq. (7).[36,46,48,49,55] Phenomenological expressions for $l_{s,\mathrm{ph}}^{-1}(T)$ were suggested for spinon-phonon Umklapp processes in $S = 1/2$ chains[46,49] and two magnon - one phonon scattering events in two-leg $S = 1/2$ ladders.[36] A theory for the spin thermal conductivity in $S = 1/2$ chains, taking into account spinon-phonon Umklapp scattering, was developed in Ref. 60. In this work, the transport in integrable systems with perturbations that weakly violate the conservation laws is considered. The presence of both spinon-spinon Umklapp processes and spinon-phonon scattering was demonstrated to lead to an exponential decrease of $\kappa_s(T)$ with increasing temperature, in apparent agreement with $\kappa_s(T)$ calculated from experimental data for Sr_2CuO_3. Spinon-phonon scattering in combination with impurity scattering in $S = 1/2$ chains was theoretically analyzed in Refs. 58,59. Three regimes with different temperature dependences for the thermal conductivity were predicted: At low temperatures it is expected that $\kappa_s(T) \propto T^2$. At intermediate temperatures, $\kappa_s(T) \propto 1/T$, and at high temperatures, κ_s is expected to be constant. The experimental values for $\kappa_s(T)$ of Sr_2CuO_3, presented in Ref. 48, seem to approach the predicted high-temperature constant value but, unfortunately, the temperature range covered by these measurements does not extend to high enough values in order to verify the predicted $\kappa_s = const$ satisfactorily.

The role of phonons is not restricted to serving as a reservoir for the exchange of energy and momentum with the quasiparticles of the spin system in the related scattering processes. First of all, a non-vanishing interaction between the lattice and the spin system is necessary for the very observability of κ_s in a typical thermal conductivity experiment, where the heat flux is first introduced into the phonon subsystem and then redistributed between phonons and spin excitations.[61] Since in an experiment probing the thermal conductivity, the spin excitations interact with phonons which are

not in equilibrium but have a nonzero net momentum along the temperature gradient, these interactions lead to a redistribution of momentum between phonons and spin excitations. If the scattering between phonons and spin excitations dominates over all other processes which lead to scattering within the spin systems (defects and Umklapp-processes), the resulting drag effects may modify κ_s. The influence of such drag effects on the thermal conductivity of conventional (3D) FM and AFM systems was discussed in Refs. 62,63. Depending on the relative strengths of magnon-phonon, magnon-defect, and phonon-defect scattering, and on the type of defects (magnetic or nonmagnetic), complex $\kappa(T)$ variations were predicted. Recently, the problem of spin drag has theoretically been addressed for spin ladders.[64] It was shown that spin-phonon drag effects modify both κ_{ph} and κ_s and also cause interference effects which are taken into account by the introduction of $\kappa_{s,\mathrm{ph}}$. With respect to experiment, no comparison of experimental data with spin-phonon drag predictions have been published up to now.

2.3. Influence of a magnetic field

According to recent theoretical work, an external magnetic field can modify κ_s not only because it changes the spectrum of magnetic excitations but also via so-called magnetothermal corrections.[65,66] In general, the heat current j_E and the magnetization current j_M are related to the temperature gradient ∇T and the magnetic field gradient ∇B by

$$\begin{pmatrix} j_M \\ j_E \end{pmatrix} = \begin{pmatrix} L_{MM} & L_{ME} \\ L_{EM} & L_{EE} \end{pmatrix} \begin{pmatrix} \nabla B \\ -\nabla T \end{pmatrix}. \tag{8}$$

In zero magnetic field, $L_{EM} = L_{ME} = 0$ and hence, the coefficient L_{EE} is equivalent to the thermal conductivity κ_s (in the following only the magnetic contribution to the heat transport is considered). In magnetic fields, the off-diagonal elements in (8) may be nonzero, and this leads to a number of interesting effects. For example, by analogy with the Seebeck effect in electric conductors, where the heat flux induces an electric voltage along the direction of the flux, j_E is expected to induce a gradient of magnetic induction in magnetic systems. A number of interesting predictions for magnetothermal effects in $S = 1/2$ chain compounds which fulfill the XXZ-model conditions, can be found in recent work in Refs. 65,25,67. At present, no experimental results on magnetothermal effects in spin chains are available, mainly because of considerable practical difficulties in carrying out such experiments.[65]

Nonzero off-diagonal elements in (8) also modify the thermal conductivity κ_s of the spin system.[25,26,66] Since heat transport experiments are

normally done under the condition of $j_M = 0$, it follows from the definition of κ in Eq. (4) that, for $B \neq 0$,

$$\kappa_s = L_{EE} - \frac{1}{T} \frac{L_{EM}^2}{L_{MM}}. \tag{9}$$

The second term on the right-hand side of Eq. (9) represents the magnetothermal correction, which was theoretically investigated in detail in Refs. 25,66. Nontrivial dependences of these corrections on temperature, magnetic field and the anisotropy parameter Δ in (3) were predicted. Unfortunately, an experimental evidence for magnetothermal corrections is still missing. Most of the good physical realizations of the 1D spin model systems discussed above, such as Sr_2CuO_3, are not suitable for this type of experiments, because of the extremely large exchange constants with J/k_B of the order of 10^2-10^3 K. Available laboratory magnetic fields are much too small to influence such systems in any significant way. Moreover, Shimshoni et al.[60] argued against the existence of these corrections in real materials because the conservation of the total magnetization may be broken by, e.g., spin-orbit coupling. In their paper, also the influence of magnetic field on the spin thermal conductivity of $S = 1/2$ chains was addressed. Complex fractal-like dependences of κ_s on the magnetization, resulting from field-induced variations of spin-phonon Umklapp scattering, were predicted.

The authors of Ref. 66 studied the relation between the thermal Drude weight D_{th} and the spin Drude weight K_s

$$\frac{D_{\text{th}}}{K_s} = L_0 T, \tag{10}$$

which is analogous to the celebrated Wiedemann-Franz law for electrical conductors. The behavior of the parameter L_0 in different parts of the phase diagram of the $S = 1/2$ XXZ chain was investigated. The relation between the heat conductivity and the spin conductivity was tested experimentally in studies of the $S = 1/2$ chain compound Sr_2CuO_3 and the $S = 1$ chain compound $AgVP_2S_6$, respectively. In Fig. 4, we show the comparison of the energy diffusion constant $D_E(T)$ obtained from the zero-field thermal conductivity measurements,[49,51] and the spin diffusion constant $D_S(T)$ established by NMR experiments.[68,69] For Sr_2CuO_3, both transport parameters show similar temperature dependences and differ by a factor close to 2. Also for $AgVP_2S_6$, D_E and D_S adopt similar absolute values and exhibit very similarly shaped temperature dependences. Earlier theoretical work[5,6,70] for $S = 1/2$ and $S = 1$ chains and the recent calculations for $S = 1$ chains,[35] indeed, predict values of the ratio D_E/D_S in the interval between 1.4 and 3 at high temperatures.
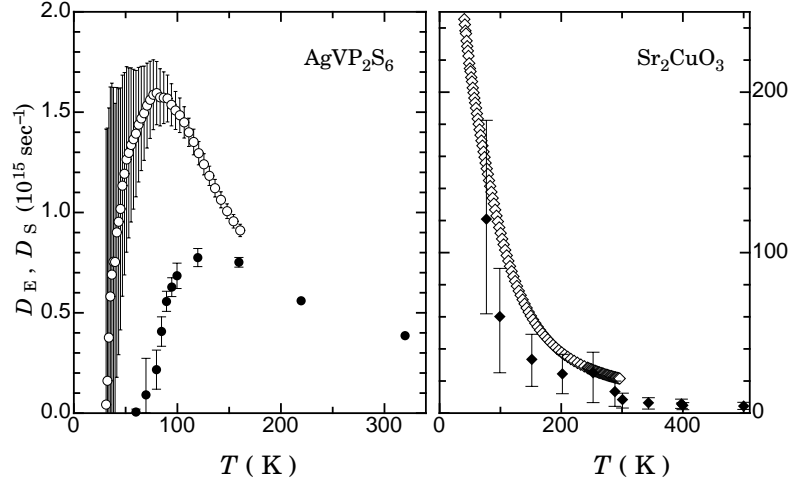
Fig. 4. The energy diffusion constants $D_E(T)$ (open symbols) of Sr_2CuO_3 and $AgVP_2S_6$, estimated from thermal conductivity data,[49,51] and the spin diffusion constants $D_S(T)$ (solid symbols) from NMR measurements[68,69] (from Ref. 51).

3. SUMMARY AND OUTLOOK

Recent experimental studies accumulated a considerable amount of evidence for heat transport via magnetic excitations in paramagnetic one-dimensional spin arrays. In some cases, particularly for $S = 1/2$ spin chains, the spin thermal conductivity is rather large, consistent with theoretical predictions which claim a ballistic form of transport. Magnetic defects were identified as one of the important sources for the scattering of spin excitations. The experiments also suggest that spin-phonon scattering is very effective in reducing the energy flow, especially at high temperatures. Recent measurements provided some support for diffusive heat transport in 1D spin systems exhibiting a gap in the excitation spectrum. Nevertheless, the situation is far from being clear, analogous to a similar controversy in the theoretical sector. Special analyses of experimental data revealed a link between the heat conduction and the spin transport in spin-chain systems.

In spite of the experimental progress in certain areas, a number of problems could not yet be solved. One of the central issues in current theoretical studies is whether the transport in spin chains with a gap in the excitation spectrum is ballistic or diffusive. The available experimental data sets do not provide enough solid evidence in favour of either of these expectations. The number of suitable materials that were studied so far, is simply too small. For example, only two $S = 1$ chain compounds were investigated. In both

materials, the concentration of magnetic defects was relatively high, leaving the possibility that intrinsic features of the thermal conductivity are masked. Also for the probed spin-ladder materials, the experimentally observed large heat flow carried by spins does not seem to contradict the possibility of diffusive transport governed by intrinsic interactions. In order to clarify this situation, more experimental work is needed.

Concerning the integrable spin systems with gapless excitation spectra, the most important problem is to establish, how the spin thermal conductivity is affected by various possible integrability-breaking perturbations, such as dimerization, frustration, weak interchain coupling, next-nearest-neighbor interactions, anisotropic interactions, various types of disorder, and coupling to phonons. Very little experimental work has been done in this direction. Even for the most extensively studied case of scattering by defects, the T - and k-dependence of the corresponding scattering rate is not yet established unambiguously. For progress in this direction, model materials that allow for a controlled alteration of different perturbations are required.

In spite of the rich variety of phenomena predicted by theory, very little experimental work has been done on the influence of magnetic fields on the spin-carried heat conduction in 1D spin systems. Progress in this area requires materials with weak intrachain exchange and yet much weaker interchain interactions. Besides variations in the thermal conductivity, a number of interesting new features in magnetothermal transport are expected to be observed.

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Thermal conductivity in spin-chain materials

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